APPLICATIONS OF FUNCTIONALIZED SINGLE-WALLED CARBON NANOTUBES

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Introduction

The outstanding materials properties of single-walled carbon nanotubes (SWNTs) have increased the level of interest in their applications. However, many of the potential applications of SWNTs are hindered by the difficulties in their processing. The chemical functionalization of SWNTs will play a key role in the realization of the promise of this material. The solubilization of SWNTs by attachment of long-chain molecules to the open ends of the nanotubes was the first step in brining SWNTs into the realm of molecular chemistry.[1] Rapid progress in development of methods for covalent attachment of various organic groups,[2-6] quantum dots[7] and biological molecules[8] has broadened the opportunities for applications of SWNTs. With the advancement in the chemistry of SWNTs it is now possible to tailor the electronic and chemical properties of SWNTs.[9,10]

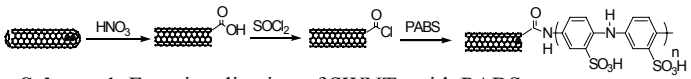
Some of the important issues addressed by the chemistry of SWNTs involve dissolution of SWNTs and bundle exfoliation. The chemical functionalization of SWNTs has been shown to increase their solubility in organic solvents and facilitate their processing.[1,11,12] It has also been demonstrated that the chemical functionalization affects the SWNT rope size and results in exfoliation into smaller bundles and individual nanotubes. These issues are especially important for the fabrication of high-performance composite materials, controlled assembling of molecular electronics and development of ultra-high sensitive sensor devises.

Here, we outline chemical approaches to functionalized SWNTs with an emphasis on their application for high-performance composites and biosensors.

Functionalization of SWNTs with oligomers and polymers

SWNTs are considered to be the ideal reinforcing fibers due to their exceptional mechanical, electronic and thermal properties, low density and high aspect ratio. However, the incorporation of SWNTs into the polymer matrix is often problematic due to the chemical inertness of SWNTs. The covalent functionalization of SWNTs is a valuable route towards the development of high-performance composites. It provides homogeneously dispersed SWNTs incorporated in the polymer and a strong interfacial bonding between the polymer and SWNTs. We have applied chemically functionalized SWNTs to prepare a number of SWNT-polymer composite materials.

In one approach, poly (m-aminobenzene sulphonic acid), PABS, a conducting water soluble polymer, was covalently attached to chemically functionalized SWNTs (Scheme 1).



Scheme 1. Functionalization of SWNTs with PABS.

AFM analysis has shown that the PABS-functionalized SWNTs exist in small bundles of 2 to 6 nanotubes (Figure 1). The graft co-polymer (PABS-SWNTs) has high solubility in water (5 mg/ml),[12] which makes the material especially attractive for biological applications. In one study, PABS-funcionalized multi-walled carbon nanotubes have been used as a substrate for neuron growth and have shown an ability to control the neurite outgrowth.[13]

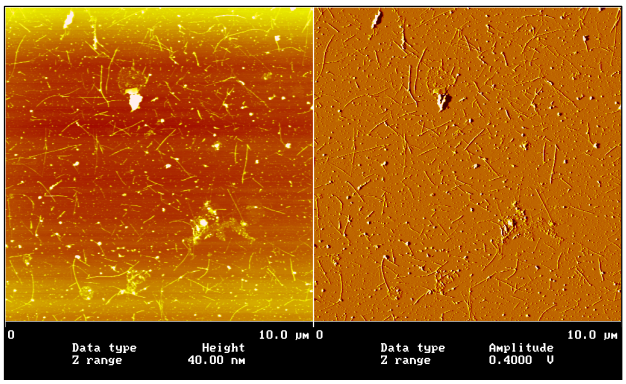
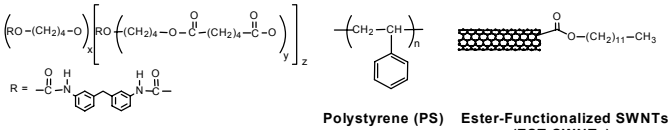


Figure 1. AFM image of SWNT-PABS showing bundles of 4-6 SWNTs.

In another study we have prepared SWNT-reinforced polyurethane (PU) and polystyrene (PS) membranes.[14] In our experiments we have used as-prepared (AP)-SWNTs and soluble ester-functionalized SWNTs (s-SWNT-$COO(CH_2)_{11}CH_3$, EST) in order to study the effect of the nanotube functionalization on the performance of the SWNT composites.



The membranes fabricated by electrospinning of the ester-functionalized SWNT-PU composite have shown enhanced mechanical properties (Table 1).[14] The increased strength exhibited by the polyurethane-SWNT-ester composites, may be due to improved dispersion of the SWNTs, but could also be a response to the polar functionalities in the SWNT-ester groups, to the opportunities offered by hydrogen bonding sites between the polymer and matrix or to amidation reactions between free amine in the polyurethane and the ester functionality in SWNTs.

Table 1. Mechanical Properties of Electrospun PU Membranes.

Electrospun membrane	Tensile strength, MPa	Tangent modulus, MPa
PU	7.02	6.96
AP-SWNT-PU*	10.26	21.86
EST-SWNT-PU*	14.36	24.32

* the SWNT:PU weight ratio is 1:100.

Functionalization of SWNTs with biomolecules

The functionalization of SWNTs with biological molecules is a relatively new direction in exploring the chemistry of SWNTs for biosensor applications. While both covalent[8,15,16] and non-covalent functionalization[17,18] with proteins, enzymes and DNA has been attempted, the covalent approach provides better stability and reproducibility of the devices fabricated from these materials.

One approach for covalent binding of proteins and enzymes utilizes the diimide-activated amidation of carboxylic acid-functionalized carbon nanotubes. We have functionalized purified SWNTs, produced by the arc-discharge method, with bovine serum albumin (BSA) as schematically illustrated in Scheme 2. The SWNT

purification process involves reflux of SWNTs in HNO_3, which terminates the open nanotube ends with carboxylic acid groups. The carboxylic groups can further undergo an amidation reaction with the amino acids of the protein.

EDC – 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride

Scheme 2. Synthesis of BSA-functionalized SWNTs.

The BSA-functionalized SWNTs were separated from the free BSA molecules by dialysis against deionized water for 5 days. A typical AFM image of the BSA-functionalized SWNTs is given in Figure 3.

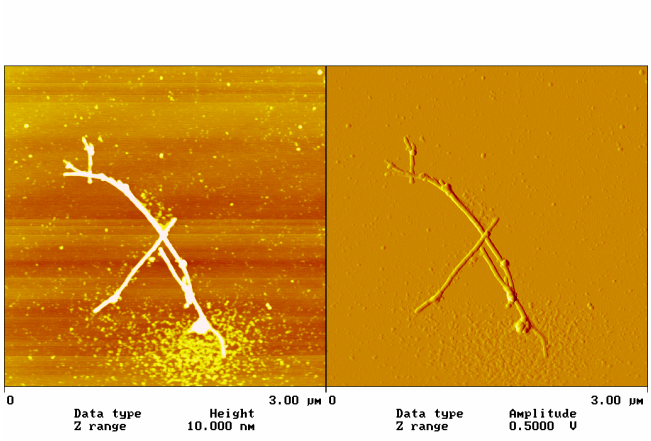


Figure 3. AFM image of BSA-functionalized SWNTs.

In order to test the biological activity of the attached the nanotubes BSA, the functionalized SWNTs were incubated in a solution of anti-BSA, developed in rabbit, for 1 hour to obtain a specific antibody-antigen interaction. The material was washed 5 times with a buffer solution (pH=7.4) and exposed to FITC-conjugated anti-rabbit IgG- for 20 min. Detection of analyte binding to the functionalized SWNTs was then performed by fluorescence and phase contrast microscopy (Figure 4).

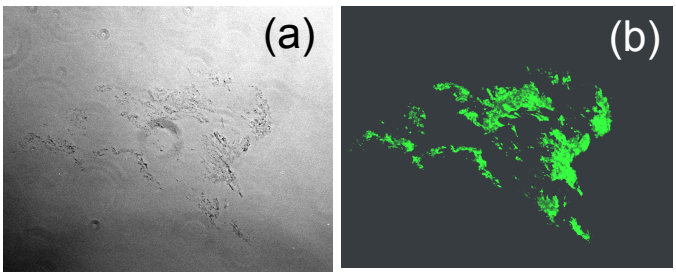


Figure 4. Phase contrast (a) and fluorescent (b) images of BSA-functionalized SWNTs.

The fluorescent image (Figure 4b) confirms the successful interaction between the BSA-functionalized SWNTs and the FITC-conjugated secondary antibody, which is an indication for the retained biological activity of the protein after the attachment to SWNTs. The fluorescent image reveals a feature similar to that observed in the phase contrast image (Figure 4a). A control test with non-functionalized SWNTs incubated in FITC-conjugated anti-rabbit IgG resulted in a dark image, which confirming the specific interaction between the BSA-functionalized SWNTs and anti-BSA. These specific interactions may be used for development of biosensors and controlled assembly of ordered nanostructures.

Conclusions.

The chemistry of SWNTs offers considerable scope for development of functional materials, structures and devices based on SWNTs. Further advance in our understanding the chemistry of SWNTs will make it possible to take full advantage of the remarkable properties of these materials and will help to tailor the properties of SWNTs for particular applications.

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